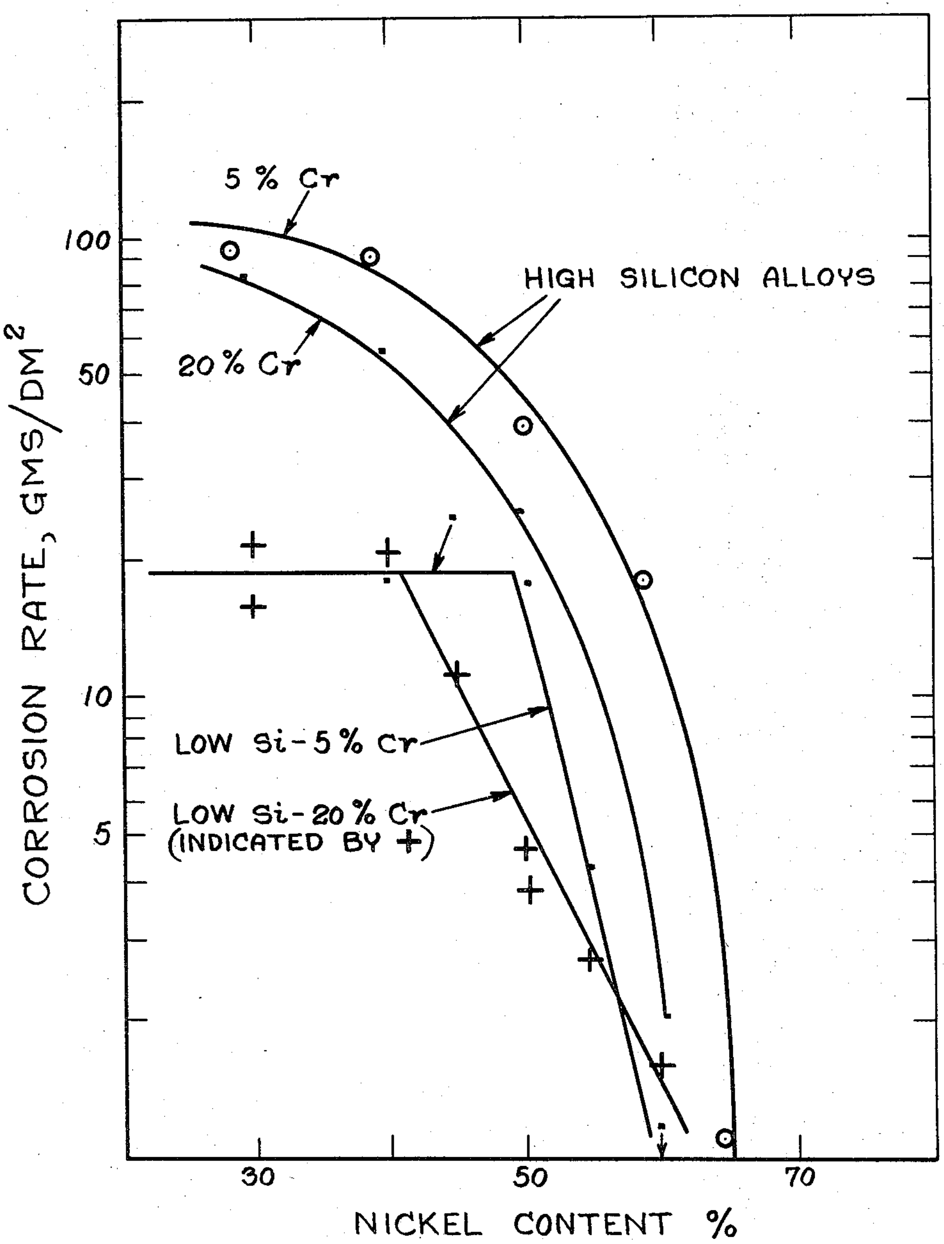
Jan. 5, 1971 G. R. RUNDELL ET AL 3,552,950
HIGH TEMPERATURE CORROSION RESISTANT Fe-G-Ni-Mn ALLOY
Filed June 14, 1967 5 Sheets-Sheet 1

Fig. 1.



CORROSION RATES OF SIMPLE FE-CR-NI ALLOYS AS A FUNCTION OF NI, CR AND SI.

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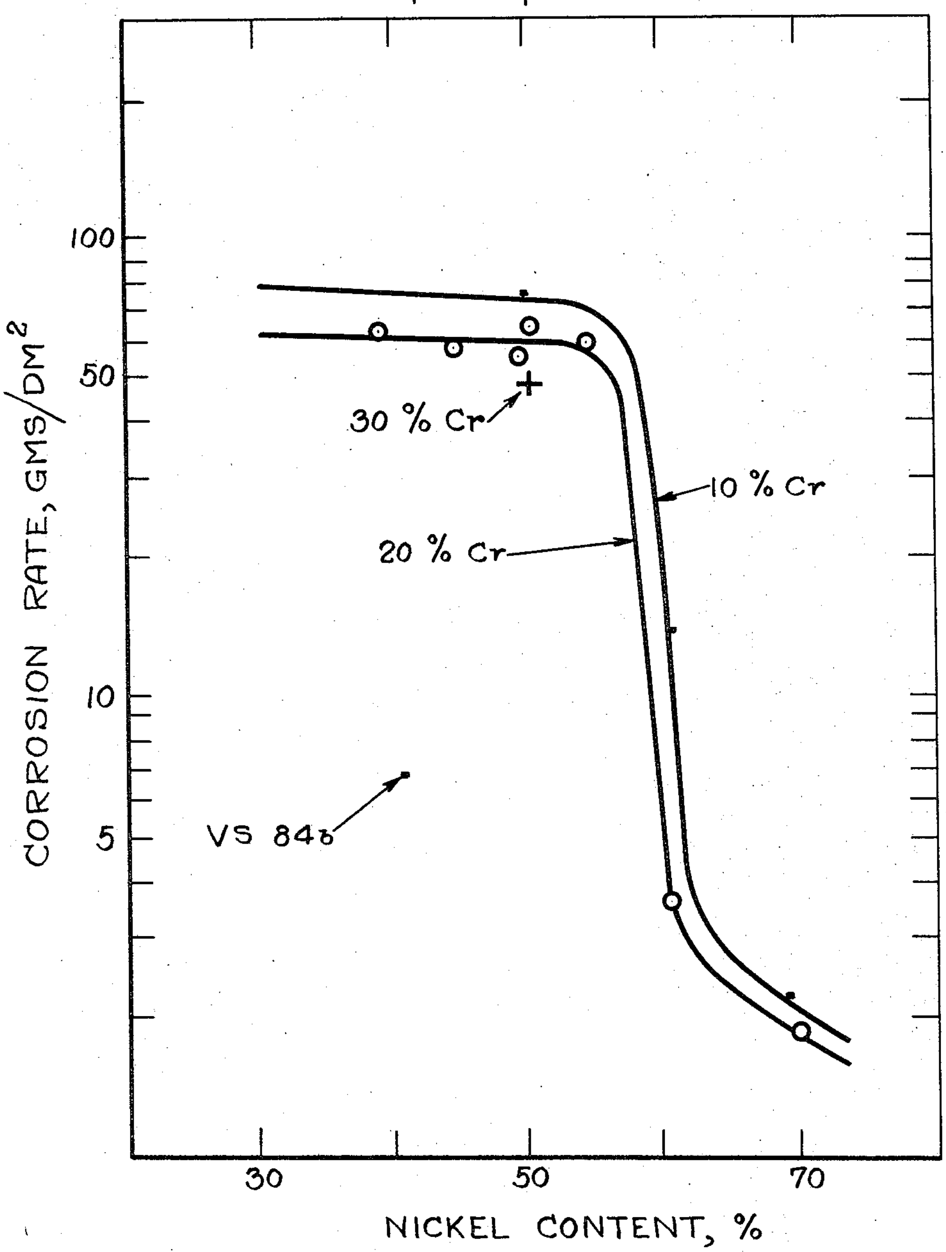
Fig. 2.



CORROSION RATES OF LOW SILICON FE-CR-NI ALLOYS CONTAINING TITANIUM AND ALUMINUM

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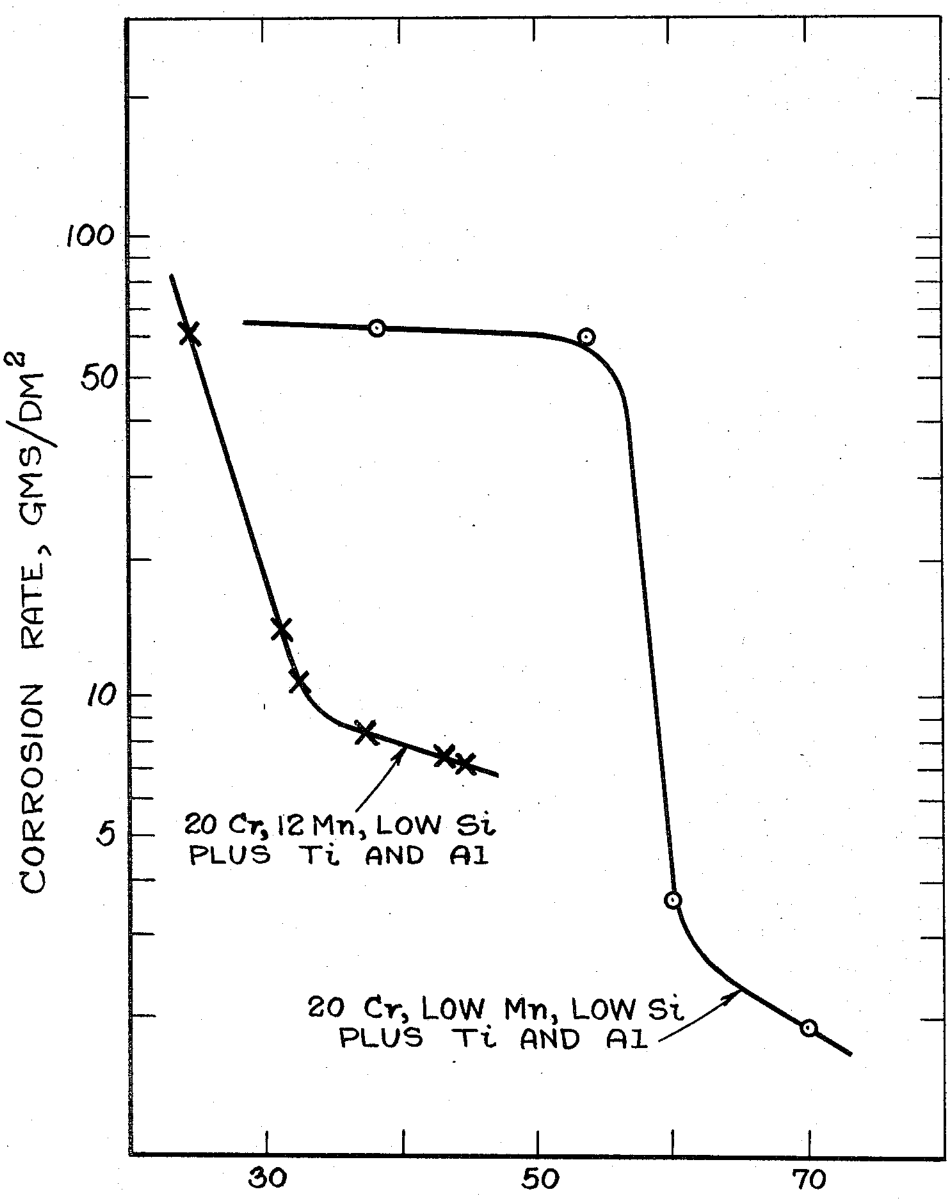
Fig. 3.



EFFECT OF 12 MN ON CRITICAL NICKEL CONTENT OF NI-FE-CR ALLOYS HARDENED WITH TI AND Al

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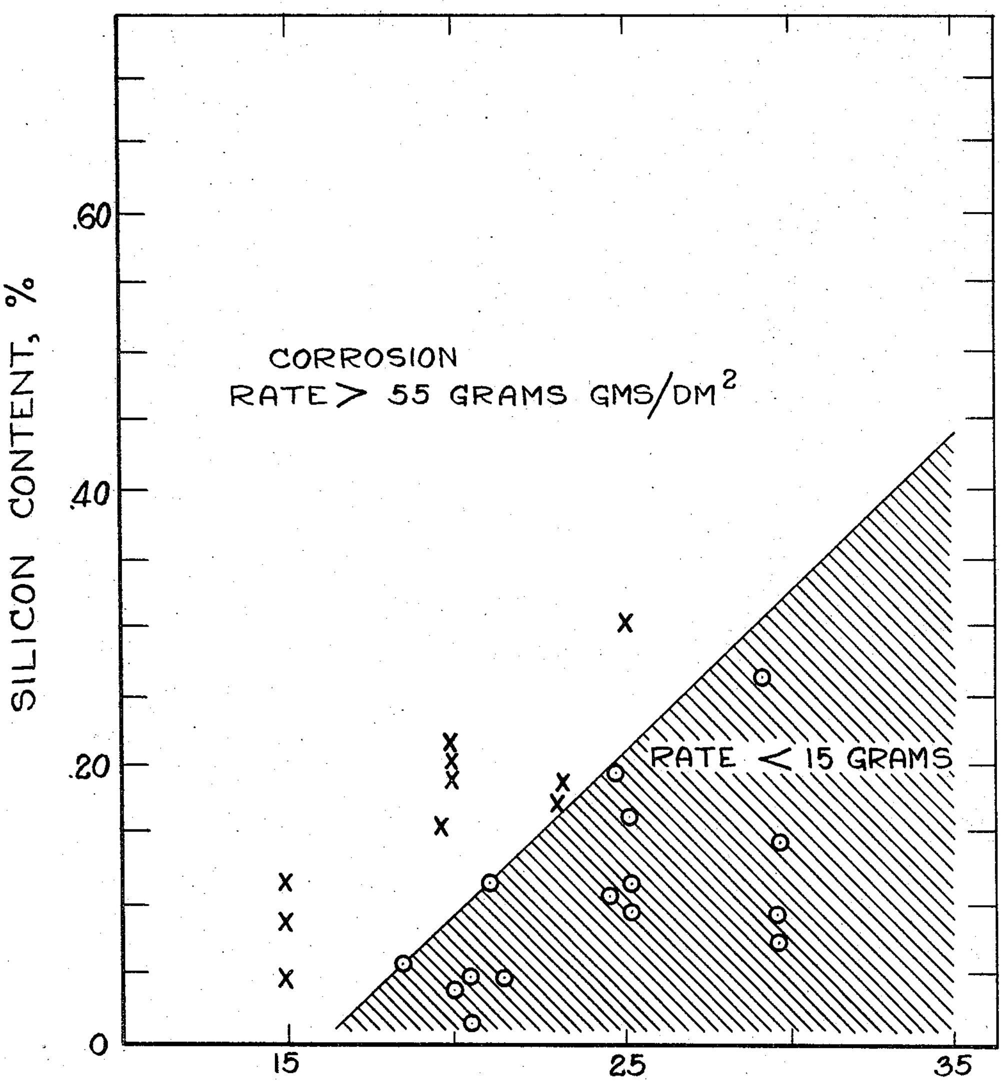
Fig. 4.



RELATIONSHIP OF CHROMIUM AND SILICON CONTENTS ON CORROSION BEHAVIOR OF FE-NI-CR-MN ALLOYS CONTAING TITANIUM AND ALUMINUM.

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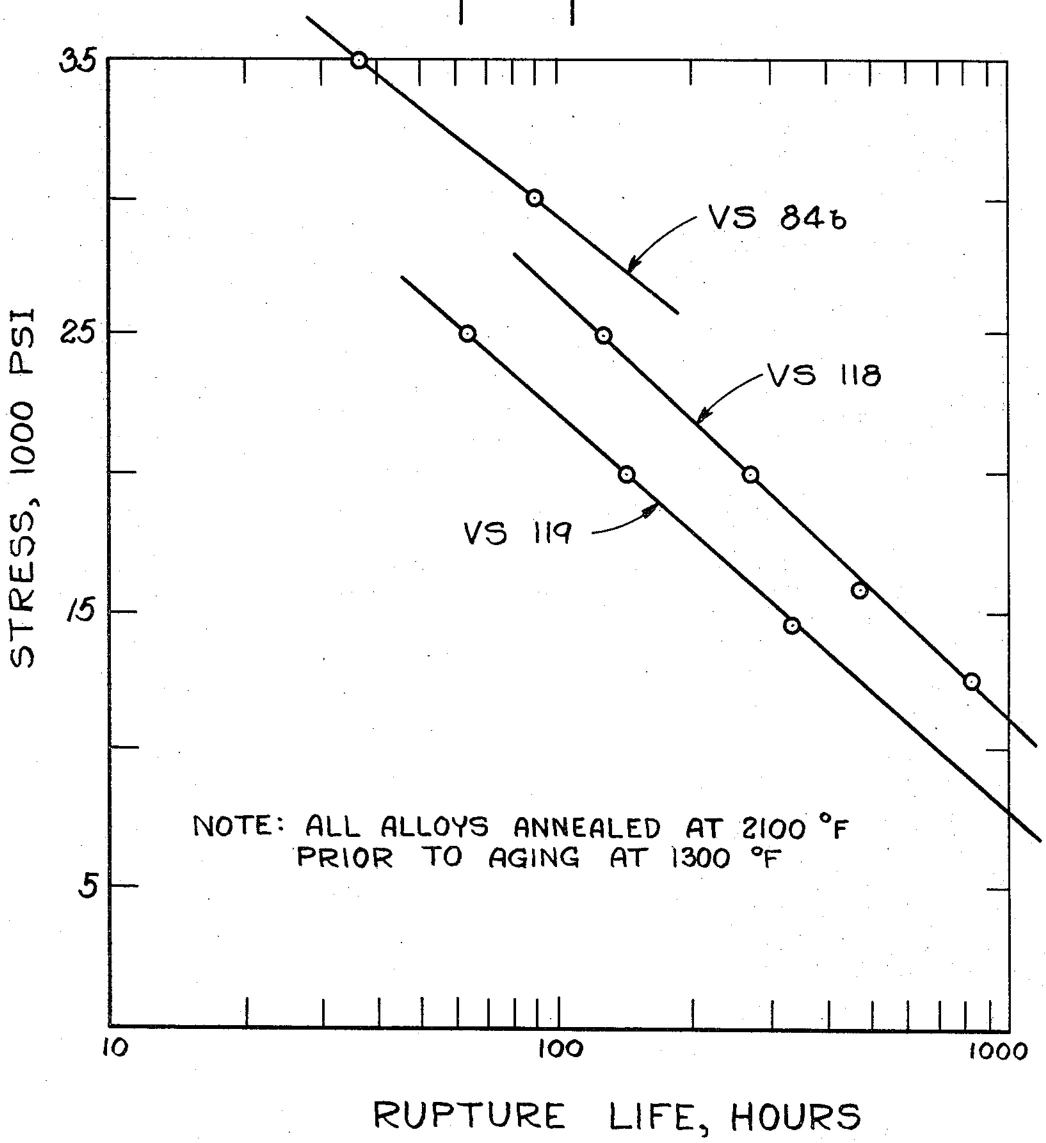
Fig. 5.



CREEP-RUPTURE CURVES OF 12 MN, 20 CR, 40 NI, 2 TI, 1 AL ALLOYS AT 1350 °F

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HIGH TEMPERATURE CORROSION RESISTANT Fe-G-Ni-Mn ALLOY

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Int. Cl. C22c 19/00, 39/02
U.S. Cl. 75—122 5 Claims

ABSTRACT OF THE DISCLOSURE

Age hardenable, austenitic alloy characterized by high elevated and ambient temperature hardness, strength and corrosion resistance, particularly adapted for internal combustion engine valves, and consisting essentially of about: 20–70% nickel, 4–20% manganese, 12–40% chromium, up to 0.5% carbon, up to 0.3% nitrogen, up to 0.6% silicon, up to 5% molybdenum, up to 6% titanium, up to 4% each of aluminum and copper, up to 0.2% boron, balance substantially iron.

This invention pertains to high temperature, corrosion resistant, age hardenable, austenitic alloys, and more particularly to an essentially medium to low carbon, low silicon, nickel-manganese-chromium-iron alloy of this type, preferably containing aluminum and titanium as age hardening elements, and wherein manganese is present in substantial amount along with nickel in critically restricted amount for imparting high elevated temperature corrosion resistance to the combustion products of leaded gasoline fuels.

For a number of years past, an alloy steel commonly known as 21–4N has been widely used for automotive exhaust valves. This steel nominally contains about 21% chromium, 10% manganese, 4% nickel, 0.5% carbon, 0.4% nitrogen, and the balance substantially iron. The steel is hardened by the precipitation of carbides and nitrides, and is characterized by unusually high tensile strength and hardness for an austenitic alloy. In addition it has good resistance to corrosion in the combustion products of leaded gasoline fuels.

It is an object of the present invention to provide an alloy which is an improvement over the 21–4N steel as regards corrosion resistance to the combustion products of leaded fuels and which in other respects possesses properties comparable thereto.

There are a number of requirements to be met by an alloy or alloy steel to render it suitable for use in internal combustion engine valves and valve parts. Such an alloy should be austenitic for reasons of strength at valve operating temperatures on the order of 1200–1600° F. Also the austenitic alloy should be hardenable by precipitation of a stable phase such as carbides or intermetallic compounds to provide resistance to wear and to indentation. Also the alloy must have adequate corrosion resistance to the combustion products of leaded engine fuels.

Inconel 750 has a corrosion rate in molten lead oxide of less than 3.0 gram per sq. decimeter, but its cost is several times that of 21–4N steel which has a corrosion rate of about 20.0 gms./dm.^{2}. As shown below the alloy of the present invention has a corrosion rate in molten lead oxide of about 10.0 gms./dm.^{2}, which places it between the iron-base alloy, 21–4N, and the nickel-base alloy, 750.

The addition of tetraethyl lead to increase the octane rating of gasoline fuels has magnified the problems of hot corrosion to the extent that the usefulness of valve alloys is judged by the corrosion resistance in pure lead oxide. A technique for testing alloys in this regard has been carefully specified in recent years, including the grade and manufacture of the lead oxide and the crucible in which such tests are conducted, specimen preparation, method of testing, and also the procedure for removing the corrosion products and calculating the corrosion rates. In practice, a specimen blank about ½ inch long is cut from .444 inch centerless ground bar. The blank is surface ground on both ends to a length of .444 inch, and is finished by hand grinding on dry 240 grit paper over the complete surface. The specimen is measured, degreased in methanol, and weighed to the nearest tenth of a milligram. It is then placed in a small magnesia crucible, covered with 40 grams of lead oxide, heated to a temperature of 1675° F., and held for an hour. After cooling to room temperature the specimen is broken out of the lead oxide, scraped to remove the loose lead oxide, and immersed in a molten solution of caustic soda and soda ash (1075 to 1100° F.) for several minutes. The sample is then cleaned by wire brushing and reweighed to determine the weight loss. This is divided by the original sample area to obtain the corrosion rate. Although the test is arbitrary, it has been found that corrosion rates correlate well with laboratory and field engine tests.

In reviewing the published literature, it is well to keep one fact clearly in mind. Many of the lead oxide corrosion test results of the published literature, were conducted in clay crucibles rather than magnesia crucibles. Tests conducted in clay crucibles result in corrosion rates which are about one fifth those for tests conducted in magnesia crucibles. All of the corrosion tests, the results of which are presented below in this application, were conducted in magnesia crucibles.

In the accompanying drawings:

FIG. 1 is a graphical showing of the corrosion rate in molten lead oxide of the various iron-chromium-nickel alloys, with both high and low silicon contents.

FIG. 2 is a similar graphical showing of other iron-chromium-nickel alloys containing titanium and aluminum as age hardening elements.

FIG. 3 is a similar graphical showing of other iron-nickel-chromium alloys which also contain manganese as well as titanium and aluminum in varying amounts.

FIG. 4 is a similar graphical showing of various iron-nickel-chromium-manganese alloys which contain titanium and aluminum.

FIG. 5 is a graphical showing of the elevated temperature, creep-rupture properties of an alloy according to the invention and of the analysis set forth therein.

In the course of the research resulting in the present invention, a large number of experimental alloys were melted and tested as identified and discussed below. These experimental alloys were tested for corrosion resistance in the cast or in the wrought condition, as hereinafter indicated. Those alloys tested in the wrought condition were solution annealed at 2100° F. and aged at 1300° F. prior to testing. Those in the cast condition were given an age hardening treatment at 1300° F. if they contained hardening elements, and were tested with no heat treatment if they did not contain hardening elements.

One objective of the research program resulting in this invention was to survey the corrosion behavior of simple Fe-Cr-Ni alloys which were treated essentially as ternary alloys, in order to determine a suitable base composition for further work.

Alloys were made with nickel contents in the range 20 to 75% and chromium contents in the range 5 to 30%. Both elements were varied independently of the other except that combinations of nickel and chromium were avoided that did not produce fully austenitic alloys. Silicon and manganese contents consistent with normal steelmaking practice (.2 to .3% and .3 to .4%, respectively) were included.

As the tabulation of the following Table I indicates, nickel was found to have a beneficial effect on corrosion resistance at all levels of chromium for alloys tested as above described. The effect of chromium was not consistently beneficial, except at one level of nickel, 60%. In no case did an alloy containing 50% or less nickel have good corrosion resistance.

TABLE I.—EFFECT OF NICKEL AND CHROMIUM ON CORROSION RATES OF SIMPLE Fe-Cr-Ni CAST ALLOYS (C 0.05% MAX., RESIDUALS NIL)

[Corrosion rate, gms./dm.^{2} at indicated nickel and chromium contents]

	Cr content, percent					
	5	10	15	20	25	30
Nickel content, percent:						
20		68.9	39.4	50.6	48.0	
30	93.6	53.3	30.9	80.3	71.8	70.7
40	90.9	70.1	48.4	56.0	83.2	76.8
50	38.6	37.6	31.5	25.4	35.2	28.1
60	17.7	17.2	17.5	2.03	1.44	1.65
65	1.07	1.21	10.8	1.36	1.03	
70	.29	3.84	.98	.91		

The corrosion rates of the 5 Cr and 20 Cr alloys are plotted as a function of nickel content in the upper two curves of FIG. 1, and serve to indicate the potent effect of nickel on corrosion resistance.

One unsettling aspect of the above data is the high corrosion rates for low nickel-high chromium alloys. The rates were considerably higher than would be anticipated from the corrosion rate of commercial alloys, such as 21–4N. Since it appeared that the silicon content of the above alloys was responsible for the high corrosion rates, a series of 5% and 20% chromium alloys at various nickel contents containing low silicon, less than 0.1%, were melted and tested for corrosion resistance as above for comparison with high silicon alloys. The results are given in the following Table II, wherein all alloys were tested in the cast condition. These data also also shown graphically in FIG. 1.

TABLE II.—EFFECT OF SILICON ON CORROSION RATES (C <0.05%; Mn 0.3-0.4%; RESIDUALS NIL)

Alloy code		Nominal comp., percent		Corrosion rate, gms./dm.^{2}	
High silicon (.25%)	Low silicon (<.1%)	Ni	Cr	High silicon	Low silicon
VS 2	VS 66	40	5	90.9	18.2
VS 3	VS 68	50	5	38.6	17.2
VS 4	VS 70	60	5	17.7	.2
VS 28	VS 71	40	20	56.0	20.6
VS 29	VS 73	50	20	25.4	3.9
VS 30	VS 75	60	20	2.03	1.5

As shown in the tabulation, all of the alloys with less than .1% silicon have lower corrosion rates than their higher silicon counterparts. It is also evident that nickel overshadows the effects of chromium and silicon on corrosion resistance as shown in FIG. 1, wherein it is further seen that an increase in chromium from 5 to 20% displaces the curves to the left (to lower nickel) by about 5%. An increase in silicon from about .1 to .25% has an opposite and greater effect.

Finally, it may be noted that low-silicon alloys do not exhibit increasing corrosion rates with decreasing nickel below about 40%. This appears to be fundamental to alloys of low silicon, and is indicated by the horizontal extension of the low silicon graphs to the left in FIG. 1 below the 40% Ni level, which implies a maximum corrosion rate of about 16 to 22 grams for Fe-base, Fe-Cr-Ni alloys. According to this figure, the only way of achieving lower corrosion rates is to increase the nickel content above 40%.

As pointed out above, one of the requirements for a suitable alloy for internal combustion engine valve applications is that it be hardenable by the precipitation of a stable phase, such as carbides or intermetallic compounds. Obviously, the addition of elements to promote hardening could affect the corrosion behavior of the simple alloys having corrosion resistant properties as above described.

Accordingly a series of alloys was made with a carbon content of about ½% each, very low silicon, under 0.1%, and with a chromium content of 20%. The nickel was varied from 30 to 70%. The corrosion rates of these 20% chromium-high carbon alloys fall very close to those for similar alloys containing low carbon, as shown in Table III below:

TABLE III.—CORROSION RATES OF HIGH AND LOW CARBON ALLOYS

	Nominal comp., percent			Corrosion rate, gms./dm.^{2}
	C	Ni	Cr	
Alloy code:				
VS 71	.02	40	20	20.6
VS 73	.02	50	20	3.9
VS 75	.02	60	20	1.5
VS 89	.45	30	20	15.7
VS 90	.45	50	20	4.7
VS 91	.45	70	20	.8

The data for these high carbon alloys are included in the plot of 20 Cr-low Si alloys of FIG. 1. These data show that carbon is not detrimental in alloys containing 20% chromium. In addition, the corrosion data of these alloys lends support to the previous observation that iron-base alloys containing less than 40% nickel exhibit a characteristic corrosion rate in the range 16 to 22 grams per square decimeter. This level of corrosion resistance is no better than exists in conventional stainless steels, such as 21–4N.

A series of alloys containing titanium and aluminum for hardening was prepared for corrosion tests. These elements combine with nickel to form an intermetallic compound, $Ni_3(TiAl)$, which can be precipitated by heat treatment to increase hardness and strength. These alloys were tested in the wrought condition, with results as given below in Table IV.

TABLE IV.—CORROSION RATES OF Fe-Cr-Ni ALLOYS CONTAINING Ti AND Al

	Nominal comp., percent			Corrosion rate, gms./dm.^{2}
	Ni	Cr	Al+Ti	
Alloy Code:				
VS 77	40	20	2.8	62.5
VS 78	45	20	3.5	58.6
VS 79	50	20	3.5	56.6
VS 80	55	20	3.9	59.9
VS 81	60	20	3.4	3.6
VS 82	70	20	3.5	1.9
VS 83	50	20	3.0	65.1
VS 86	50	10	2.7	58.0
VS 87	50	10	3.7	75.0
VS 88	60	10	3.4	14.1
VS 94	50	30	2.8	49.6

The effect of nickel is shown in the first group of this series; that of chromium and hardener content, in the last group. When these data are plotted as in FIG. 2, it is readily apparent that nickel exerts the most potent effect on corrosion behavior. An increase in hardener content from 2.7 to 3.7% for alloys 86 and 87 has a moderate detrimental effect. A chromium increase of 10% was found to shift the curves slightly to the left in FIG. 2 to lower nickel. One of the striking aspects of these data is the abrupt decrease in corrosion rate between 55 and 60% nickel. The corrosion rates are not affected once the nickel content is reduced below 55%. This is evident as the flat portion of the curve near the upper left corner of FIG. 2. Also, the effect of nickel is only slightly beneficial above nickel contents of about 65%.

A comparison of FIGS. 1 and 2 indicates the effect of adding titanium and aluminum to low-silicon Fe-Cr-Ni alloys is to shift the steep portion of the curve to the right (to higher nickel contents); to make the transition from high to low corrosion rates more abrupt; and to raise the position of the flat portion of the curve to higher corrosion rates.

It is also evident from FIGS. 1 and 2 that nickel exerts the most influence on the corrosion resistance of these alloys, and it is useful to consider the effect of other elements in terms of the nickel content required for a given corrosion rate. For purposes of this invention, the term "critical nickel content" will be used to denote the nickel content required for a corrosion rate of less than 15 grams per square decimeter. For low silicon alloys the effect of adding titanium and aluminum is to increase the nickel content from 45 to about 60%.

FIG. 2 also indicates that the objective of developing an alloy of lower cost than Inconel "750," cannot be realized in Fe-Cr-Ni alloys containing titanium and aluminum, since a reduction in nickel from about 75% for Inconel 750 to 60% is not sufficient to affect the cost appreciably.

The most significant discovery leading to the development of a completely new alloy according to this invention, is the effect of manganese in lowering the critical nickel content from about 60 to 34% for alloys hardened with titanium and aluminum, as shown by the following.

A series of alloys all containing essentially constant chromium contents of 20%, with about 12% Mn, less than .06% Si, and between 3 and 4½% titanium plus aluminum were melted and corrosion tested. The corrosion rates are plotted as a function of nickel content in Graph A of FIG. 3. The critical nickel content of this series is shown about 34%, compared to 60% for a similar series without manganese, the latter as shown by Graph B of FIG. 3, copied from the 20% Cr graph of FIG. 2.

Two additional series of Mn-containing alloys were prepared with varying manganese contents. The purpose was to establish a relationship between manganese level and corrosion rate and to determine whether 12% manganese is necessary to provide the desired low level of corrosion. These data are tabulated below in Table V for alloys containing 36% nickel, low silicon, and combined titanium and aluminum in excess of 2.3%.

TABLE V

[Effect of manganese variation at 20% Cr, 36% Ni]

	Manganese content, percent	Corrosion rate, gms./dm.²
Alloy:		
VS 124	6.68	15.2
VS 125	9.40	13.1
VS 126	12.33	13.6
VS 127	15.51	13.3
[Effect of manganese variation at 25% Cr, 36% Ni]		
VS 128	4.34	63.5
VS 129	4.74	12.1
VS 130	6.19	12.9
VS 131	12.31	10.0

These data show that the minimum manganese content required for the necessary low level of corrosion is much lower than 12%. In the 36% Ni-25% Cr low Si alloys, as little as about 5% Mn is adequate. There is no further lowering of corrosion resistance when the manganese is increased above this critical level.

During the course of our investigation it appeared that low chromium alloys were somewhat less corrosion resistant than high chromium alloys. In addition our previous investigations had established, as shown above, that silicon has a detrimental influence on corrosion resistance. Consequently, the effect of silicon at various chromium contents was determined for 12% manganese alloys containing about 2–3% of titanium and aluminum, with results as shown in Table VI below.

TABLE VI.—EFFECT OF SILICON AT VARIOUS CHROMIUM CONTENTS IN 36% NICKEL ALLOYS

	Chromium content, percent	Silicon content, percent	Corrosion rate, gms./dm.²
Alloy:			
VS 121 'A'	15	.05	82.2
VS 121 'B'	15	.09	78.1
VS 121 'C'	15	.12	71.7
VS 122 'D'	20	.12	9.73
VS 122 'A'	20	.16	58.6
VS 122 'B'	20	.20	55.2
VS 131	25	.12	10.0
VS 133	25	.17	10.0
VS 135	25	.31	56.5
VS 123 'A'	30	.08	10.9
VS 123 'C'	30	.15	11.4
VS 123 'D'	30	.27	10.9

These data again confirm that silicon has a detrimental effect on corrosion resistance. For example, an increase in silicon from .12 to .16% for 20% Cr alloys increases the corrosion rate by a factor of six. A similar effect occurs for 25% Cr alloys at somewhat higher silicon. It is also shown from the low corrosion rates of all of the 30% Cr alloys, that chromium increases the amount of silicon that can be tolerated.

This is shown graphically depicted by plotting data points of high corrosion resistant and low corrosion resistant alloys as a function of silicon and chromium contents in the manner illustrated in FIG. 4. The alloys represented by the letter x have corrosion rates in excess of 55 grams/dm.²; those by open circles have rates less than 15.

The inter-relation of chromium, silicon, and corrosion behavior may be expressed in terms of the following equation:

$$\text{(1)} \qquad \text{Percent Cr} \geq 16 + 43.5\% \text{ Si}$$

If the chromium equals or exceeds the amount calculated from this equation, the corrosion rate will be less than 15 gms./dm². If the chromium is less than the amount indicated the corrosion rate will exceed 55 gms./dm².

Equation 1 is written with silicon as the independent variable. However, if chromium is to be considered as an independent variable, Equation 1 may be transposed in accordance with Equation 2 below:

$$\text{(2)} \qquad \text{Percent Si} \lesseqgtr \frac{\text{Percent Cr} - 16}{43.5}$$

It is obvious that the silicon must be less than this amount for good corrosion resistance.

In considering how generally the above relationship may be applied, reference may be had to the corrosion behavior of some of the other alloys melted and tested in the course of the present investigation. For example, alloys VS 54 and VS 55, containing 70% Ni, 10% Cr, 0.3–0.34% Si and about 2.8–3.6% Ti and Al, did not have a chromium content equal to that calculated from Equation 1, yet the corrosion resistance was very good. This serves to illustrate that chromium and silicon variations do not affect corrosion resistance independently of nickel. An alloy similar to VS 54 and 55, except for the absence of chromium, was found to have poor corrosion resistance. It is thus concluded that chromium is necessary in 70% nickel alloys hardened with titanium and aluminum. However, the amount of chromium required can be considerably lower for the 70% nickel alloys than for alloys containing less than about 40% nickel. Since the objective in practicing this invention is to provide good corrosion resistance at low cost, primary concern is with the effects of chromium and silicon at intermediate nickel contents where Equation 1 is valid.

By way of summary, it has been shown above that Fe-Cr-Ni alloys, containing substantial manganese in addition to titanium and aluminum for hardening, have useful corrosion resistance at much lower nickel contents than low manganese alloys. Our investigations have shown that good corrosion resistance is obtained at nickel contents as low as 34 percent. Additional corrosion tests of 36% nickel alloys were conducted to determine the amount of manganese required for corrosion resistance. This was found to be about 5%. Finally, it was found that silicon has a ruinous effect on corrosion resistance of 12% manganese alloys. The amount of silicon that can be tolerated increases with increasing chromium and can be predicted in the manner shown above. The test results presented above have shown that nickel, chromium and manganese are beneficial to corrosion resistance, while silicon, titanium and aluminum are detrimental. Other elements which have been included and which do not appear to influence corrosion behavior are copper and carbon.

In order to show the mechanical properties of the alloys of the invention, typical compositions according to Table VII below were wrought, solution annealed at 2100° F. and age hardened at 1300° F. for 22 or 32 hours. The aging times were selected to produce the maximum hardness obtainable at a temperature of 1300° F. The carbon contents of all alloys were 0.1% max. The alloys were found to resist rapid over-aging at this temperature, and aging times of 22 or 32 hours gave essentially equal results.

TABLE VII.—TENSILE PROPERTIES OF HIGH MANGANESE Fe-Cr-Ni ALLOYS HARDENED WITH Ti AND Al

Alloy Code VS	Nominal comp., percent						Hard. Rc	Strength, 1,000 p.s.i.		Ductility, percent	
	Ni	Cr	Mn	Mo	Cu	Ti + Al		Ult.	.2% yield	El.	R.A.
84 'B'	41	21	11			3.3	31.5	162	96	16.9	16.4
113	44	21	12			4.1	33.5	136	114	3.5	6.6
115	45	20	12		1.0	4.4	34.0	133	112	2.1	3.3
118	38	20	12		1.0	3.3	27.5	140	79	12.5	16.7
138	34	23	5			2.7	24.5	152	75	24.5	32.6
139	34	23	5	2.0		3.1	23.0	151	75	28.0	30.8
138 'B'	34	25	5			3.4	32.0	160	87	19.0	19.7

It is apparent from the above data that aged hardness varies with the hardener content (Ti+Al), the higher contents yielding the highest hardness. The yield strength varies in a similar manner. Tensile ductility tends to vary inversely with the hardener content. The manganese contents of 5 and 12 percent do not significantly affect the mechanical properties. A lower limit of Ti and Al for the alloys of this invention is dictated by the requirements of hardness and strength. Conversely, an upper limit is dictated by tensile ductility which drops off sharply with hardener contents in excess of about 4%.

Typical creep rupture properties for the alloys of the invention are given below in Table VIII for the alloys in wrought form as annealed at 2100° F. and age hardened at 1300° F.

TABLE VIII.—CREEP RUPTURE STRENGTH AT 1,350° F. OF HIGH MANGANESE Fe-Cr-Ni ALLOYS CONTAINING Ti AND Al

Alloy Code	Ni	Cr	Mn	Cu	Mo	Ti+Al	100 hour rupture strength, p.s.i.
VS 84 'B'	41	21	11			3.3	29,500
VS 118	38	20	12		1.0	3.3	26,500
VS 119	38	20	12		3.0	3.3	22,000
VS 138	34	23	5			2.7	28,000
VS 139	34	23	5	2.0		3.1	38,000

Creep-rupture strength increases with higher solution annealing temperatures (up to 2100° F.) although hardness, tensile strength, and ductility are reduced somewhat.

The significant variant of the first three alloys in the above table is copper. As shown, each addition of copper results in a substantial loss of high temperature strength. The last two alloys contain 5% manganese rather than 12 percent, and last of these also contains two percent molybdenum. Alloy VS 138, containing 5% manganese, has slightly lower strength than its high manganese counterpart, VS 84'B'. This slightly lower strength is probably due to the lower hardener content of VS 138. A comparison of VS 138 and VS 139 demonstrates the potent

strengthening effect of 2% molybdenum. This addition of molybdenum also has a beneficial effect on creep rupture ductility at 1350 and 1500° F.

In the alloys of the invention, the amount of nickel that may be replaced is about six times the manganese (both have about equal atomic weight). Only about half of the nickel otherwise required may be thus replaced. The alloys containing 5% or more of manganese and 33% or more of nickel show characteristically higher corrosion rates than nickel-base, low manganese alloys, as shown by FIG. 3. However, the higher corrosion rates of manganese modified alloys is well within a value of 12, thought to be necessary for a new alloy.

Manganese has a completely different function in the alloys of this invention than in known types of iron-base austenitic stainless steels, such as those containing low nickel, high manganese, carbon, and nitrogen. The function of manganese in such alloys is to stabilize the austenitic structure in the absence of sufficient nickel. From a consideration of the similar corrosion resistance of high manganese stainless steels such as 21–4N and ordinary stainless steels such as Type 304, it is evident that manganese is not required to impart corrosion resistance thereto. The alloys of this invention on the other hand, contain far more nickel than necessary to result in an austenitic alloy. Manganese is added for its effect on corrosion resistance alone. The amount of manganese required for good corrosion resistance is substantially less than that required to stabilize the austenitic structure of low-nickel, chromium stainless steels.

It has been shown in accordance with this invention that the addition of manganese in critical amount of about 4–5% to an alloy containing about 36% nickel, 25% chromium, 2% Ti, 1% Al, markedly improves the corrosion resistance thereof.

The prior literature indicates that increasing silicon content in chromium-nickel or in chromium-nickel-manganese stainless steels adversely affects corrosion resistance. In contrast it has been shown herein as evidenced by the data of FIG. 4 that the amount of silicon which can be tolerated increases with increasing chromium content. The importance of this relationship rests on the fact that the important raw materials used in the manufacture of alloys according to the invention generally contain substantial amounts of silicon, such that it is difficult to maintain silicon contents below about .2 percent for high chromium alloys. If low silicon raw materials, such as electrolytic chromium are used, the cost of the alloy becomes prohibitive. From a knowledge of the information given in FIG. 4, one may select chromium and silicon contents consistent with good corrosion resistance and also with economical melting practice.

Addition of certain elements which are soluble in austenite, and which are known to promote solution strengthening, are to be considered within the scope of this invention, since hardness, strength, and corrosion resistance are required. Elements such as Mo, W, and V fall into this group. Of these elements, Mo is regarded as one of the most promising, as evidenced by the creep-rupture strength at 1350° F. Addition of such elements is permissible in total amount up to about 5%.

Although the alloys of this invention have been developed for their resistance to catastrophic oxidation in the presence of lead oxide, their oxidation resistance in other environments renders them suitable for applications other then exhaust valves.

Broad and preferred range for alloys according to the invention are as follows:

	Weight percent	
	Broad range	Preferred
Element:		
C	0–.5	0–0.10
N	0–.3	0.03–0.1
Si	0–.6	<0.45
Mn	4–20	5–8
Ni	20–70	34–40
Cr	12–40	20–36
Mo, W and/or V	0–5	0–3
Ti	0–6	1.5–3
Al	0–4	0.8–1.5
Cu	0–4	0–0.5
B	0–.2	0–0.1
Bal	(1)	----------

[1] Substantially Fe.

What is claimed is:

1. An age hardenable alloy characterized in having a corrosion rate in molten lead oxide as measured in a magnesia crucible of less than about 15 grams per square decimeter, said alloy consisting essentially of up to 0.5% carbon, up to 0.3% nitrogen, up to 0.6% silicon, up to 5% in total amount of at least one metal of the group MO, W and V and combinations thereof, up to 4% copper, up to 0.2% boron, 1.5 to 3% titanium, 0.8 to 1.5% aluminum, 12 to 40% chromium with the chromium content at least equal to 16+43.5×percent silicon, 34 to 70% nickel, 4 to 20% manganese, the nickel content being selected relative to the manganese content to provide said corrosion rate, and the balance substantially iron.

2. An age hardenable alloy as set forth in claim **1** wherein the carbon content is up to 0.1%, the nitrogen content is 0.03 to 0.1%, the silicon content is less than 0.45%, the content of metal of said group is up to 3%, the copper content is up to 0.5%, the boron content is up to 0.1%, the chromium content is 20 to 36%, the nickel content is 34 to 40% and the manganese content is 5 to 8%.

3. An article for use at elevated temperature under corrosive conditions made of an alloy according to claim **1**.

4. An internal combustion engine valve made of an alloy according to claim **1**.

5. An internal combustion engine valve part made of an alloy according to claim **1**.

References Cited

UNITED STATES PATENTS

3,495,977 2/1970 Denhard et al. -------- 75—128

RICHARD O. DEAN, Primary Examiner

U.S. Cl. X.R.

75—124, 125, 128, 171, 176

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,552,950 Dated January 5, 1971

Inventor(s) Gene R. Rundell et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the drawings and printed specification, title of invention, "HIGH TEMPERATURE CORROSION RESISTANT Fe-G-Ni-Mn ALLOY", each occurrence, should read -- HIGH TEMPERATURE CORROSION RESISTANT Fe-Cr-Ni-Mn ALLOY --. Column 7, TABLE VIII, lines 52 to 62 inc., in the column headings designated "Alloy Code", "Cu" should read -- Mo --, and "Mo" should read -- Cu --.

Signed and sealed this 29th day of June 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents